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Preparation and characterization of a linear poly(4-vinyl pyridine)-*b*-polybutadiene-*b*-poly(4-vinylpyridine) using a *t*-butyllithium/*m*-diisopropenylbenzene diadduct as a dicarbanion initiator

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Abstract

A linear, nearly monodispersed poly(4-vinylpyridine)-*b*-polybutadiene-*b*-poly(4-vinylpyridine) (VBV) has been synthesized using a dicarbanion initiator. The diinitiator, comprising a 2:1 molar ratio of *t*-butyllithium to *m*-diisopropenylbenzene, was prepared at −20°C in the presence of triethylamine, amounting to 1.5 times of the *t*-butyllithium moles to ensure a difunctionality. The VBV synthesis was conducted at −80°C in a mixed THF/toluene solvent in order to circumvent the chain branching reactions arising from the −N=CH− group of the 4-vinylpyridine. The absence of chain branching under such conditions has been verified by GPC/MALL and UV analyses, and syntheses at higher temperatures are detrimental. Compared with an analogous polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS), VBV relaxes slower with a higher activation energy of relaxation. Although phase separation occurs for both VBV and SBS, VBV exhibits a different morphology having a hard domain of a droplet–cluster type. The polarity of the poly(4-vinylpyridine) not only produces a T_g higher than that of the polystyrene, but also increases the T_g of the rubbery polybutadiene phase. The relaxation mechanism deduced based on the X-method indicates that contributions to relaxation for both VBV and SBS are in such order: physical flow > domain destruction > physical untanglement. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(4-vinylpyridine)-*b*-polybutadiene-*b*-poly(4-vinylpyridine); Diinitiator; *t*-butyllithium

1. Introduction

Styrenic block copolymers such as polystyrene-*block*-polybutadiene-*block*-polystyrene type (SBS) are an important class of thermoplastic elastomers. Their formulating and processing flexibility has made their use wide, in applications such as hot melt and solvent-based adhesives. In order to provide an increased polarity providing better adhesion properties, our interest in the chemical modification of SBS has led us to study the synthesis and characteristics of poly(4-vinylpyridine)-*block*-polybutadiene-*block*-poly(4-vinylpyridine) (VBV).

While information on the synthesis of poly(4-vinylpyridine) or block copolymers having poly(4-vinylpyridine) as the last block are abundant [1–10], very little is known about the VBV triblock copolymer with a linear molecular structure analogous to a SBS triblock copolymer. A linear VBV copolymer is difficult to synthesize because of two difficulties: (1) the nucleophilicity of the N atom causes a significant amount of chain branching during the formation of the poly(4-vinylpyridine) block; and (2) the crossover deficiency from 4-vinylpyridine to butadiene makes the sequential formation of the blocks unable to yield a well-defined copolymer. The chain branching phenomenon was reported first by Luxton et al. [1], in the synthesis of the polystyrene-*b*-polybutadiene-*b*-poly(4-vinylpyridine) block copolymer, and a linear polymer not heavily contaminated with branched species has been made by Arai et al. [2,3]. Anionic homopolymerization and block copolymerization of 4-vinylpyridine at low temperatures by Varshney et al. [10] enabled high yield syntheses without chain branching. Nugay et al. [4] modified both initiator and active chain ends and avoided the occurrence of chain branching during the synthesis of poly(methylmethacrylate)-*b*-poly(4-vinylpyridine) diblock copolymers. On the contrary, the crossover deficiency caused by the difference in reactivity between two monomers has been shown by Creutz et al. [8,9] to depend upon the addition mode, temperature, and the choice of solvents and additives in the block copolymerization of 4-vinylpyridine and *t*-butylmethacrylate. In spite of these difficulties, recent advances in diinitiator techniques

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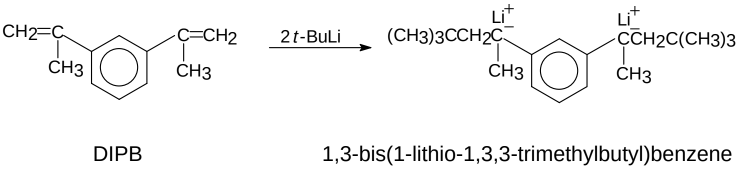


Scheme 1.

used for making telechelic copolymers have prompted us to study the possibility of utilizing a diinitiator to synthesize a VBV triblock copolymer and in the mean time ensure a linear molecular structure.

Among all the diinitiator studies [11–47], the diinitiator formed by a lithiation of *m*-diisopropenylbenzene (DIPB) using either *n*-butyllithium, *s*-butyllithium or *t*-butyllithium has gained considerable attention due to its good solubility in hydrocarbon media and the low ceiling temperature of DIPB for preventing homopolymerization. However, the association of diinitiators and the addition of polar additives affect a diinitiating process as previously pointed out by Fetters et al. [41] and Quirk et al. [42], and the formed diinitiators will have varying efficiencies and exhibit a mono-functionality under improper reaction conditions [28–30,38,39,43–47]. In this paper, our work about making an efficient diinitiator 1,3-bis(1-lithio-1,3,3-trimethylbutyl)-benzene is presented first, followed by a description of the linear VBV synthesis studies. Finally the resulting VBV is characterized and compared against an analogous SBS copolymer.

2. Experimental

2.1. Materials

Butadiene and styrene used in this work were obtained from Taiwan Synthetic Rubber Corp. (TSRC) and pretreated with activated alumina (from Alcoa Co.) prior to their use. 4-Vinylpyridine with 95% purity was purchased from Acros and treated with activated alumina prior to use. Cyclohexane obtained from TSRC has been distilled, treated with activated alumina and degassed. Tetrahydrofuran (THF), triethylamine (TEA) and hexane were purchased from Merck and pretreated with activated alumina. Reagent grade DIPB was purchased from TCI and treated with activated alumina. *t*-butyllithium (*t*-BuLi) was purchased from Acros as 15 wt% solution in hexane.

2.2. Preparation of the diinitiator

The dicarbanion initiator used for the polymer synthesis in this work was prepared by reacting *t*-BuLi with DIPB in *n*-hexane solvent. A required amount of *t*-BuLi in hexane solution was firstly charged and sealed into a glass bottle in an air-free glove box. Prescribed amounts of TEA and *n*-hexane were then added into the bottle using syringes to make a total 15 wt% solution. This sealed bottle was kept with magnet stirring in a constant temperature bath. DIPB was then added into the bottle in a dropwise manner and the solution turned red indicating the formation of the diinitiator. The extent of the DIPB reaction was determined through a measurement of double bonds using FTIR. This formed diinitiator solution was stored in a refrigerator for later use. The mechanism of the formation of the diinitiator is shown in Scheme 1.

2.3. Analysis of the diinitiator

The diinitiator was analyzed using Finnigan MAT GC/MS equipped with a ITD detector. This instrument has a DB-5 J&W capillary column of 30 m length and 0.32 mm diameter. The injection temperature was 280°C. After being kept at 80°C for 5 min, the column was heated at a rate of 6°C/min to 280°C and maintained at that temperature for another 5 min.

2.4. VBV synthesis using the diinitiator

The synthesis of VBV was accomplished in a mixed THF/toluene solvent. 300 ml of mixed solvent containing 25 vol% THF was firstly put into a 1 l pressure vessel under a slight nitrogen overpressure. The vessel content was then heated to a specified temperature prior to the addition of the required weight of the diinitiator. Afterwards, 2 g of butadiene was charged and anionically polymerized for 2 h. An additional 47 g of butadiene was then charged into the vessel, in order to continue forming a polybutadiene block of desired length. Four hours later, the temperature of the reaction system was cooled down to −80°C using an acetone/dry ice bath, and an additional 150 ml of THF was charged to increase the THF content to 50 vol%. 4-Vinylpyridine (21 g) was next charged into the reactor. The yellowish color of the polybutadienyllithium ends disappeared and the red color of newly formed poly(4-vinylpyridinyl)lithium ends appeared. The living chain ends were then deactivated after 2.5 h by the addition of methanol. The reaction solution was then poured into isopropanol and the synthesized VBV was precipitated out and dried in a vacuum oven.

2.5. Analysis of the synthesized polymer

The molecular weights and molecular weight distributions of synthesized polymers were determined by Waters

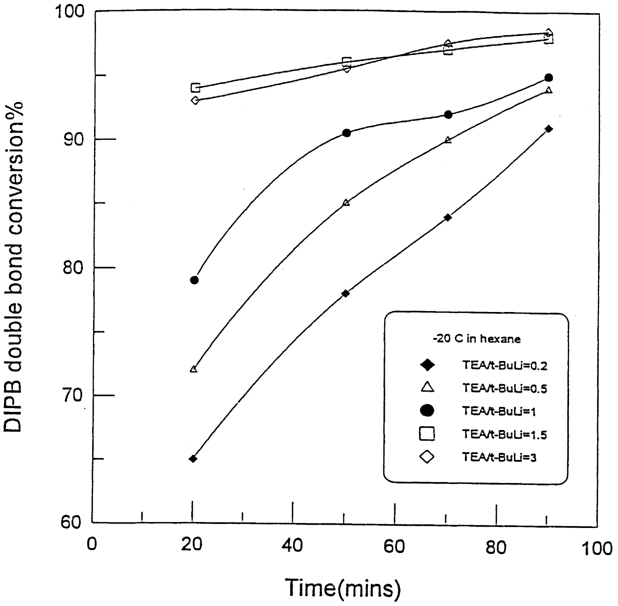


Fig. 1. Conversion of the double bonds of DIPB as a function of time (*t*-BuLi/DIPB = 2, −20°C, TEA/*t*-BuLi = 0.2 ~ 3.0, in *n*-hexane).

gel permeation chromatography (GPC) equipped with a Waters 410 differential refractive index (RI) detector and a multiple angle laser light scattering (MALL) detector. The GPC was typically operated using three Waters Styragel HR columns (10^3, 10^4, 10^5 Å) at a nominal flow rate of 1 ml/min with a sample concentration of 0.1 wt% in THF solvent. The MALL detector (miniDAWN model, Wyatt Technology Corporation) was equipped with a 20 mW semiconductor laser. The d*n*/d*c* (specific refractive index increment) of the synthesized polymer, at the same wavelength of light as the MALL, needed for the molecular weight calculation was measured by a Wyatt/Optilab DSP interferometric refractometer. The microstructure was determined by the Schimadzu FTIR-8101M spectrometer using a liquid N_2 cooled MCT detector. The spectral resolution was 2 cm^{-1}. The dynamic mechanical analysis was performed using a Rheometrics RSA II with a tensile test jig. Strain was applied to the test sample, and the corresponding stress was measured by a transducer. The test samples were of a size of $0.5 \times 8 \times 300$ mm^3.

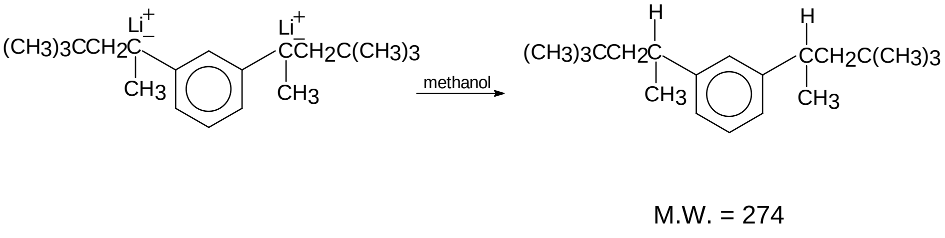
3. Results and discussion

The reaction of 2 mol of *t*-BuLi with one mole of DIPB at a temperature of −20°C, in the presence of varying amounts of TEA, has been conducted to form the 1,3-bis(1-lithio-1,3,3-trimethylbutyl)benzene diinitiator. As illustrated in Fig. 1, a conversion of the double bonds of DIPB greater than 97% after 1.5 h was achieved at a TEA/*t*-BuLi molar ratio of 1.5. A higher TEA/*t*-BuLi ratio did not increase the conversion any further. The conversion of the double bonds of DIPB was determined using FTIR spectra. The double bonds of the DIPB exhibit a peak at 890 cm^{-1}. Their conversion was calculated by comparing the absorption peaks before and after the reaction, with the intensities of both peaks being first normalized against the absorption peak of *meta*-substituted benzene at $750 \sim 810$ cm^{-1}. The formation of this diinitiator was verified through the existence of its hydrocarbon derivative after hydrolysis (Scheme 2).

Our GC/MS confirmation of the molecular weight of this hydrocarbon derivative is shown in Fig. 2. The peak in the GC chromatogram was identified, using the MS spectrometer, as the hydrocarbon derivative having a parent ion of *m*/*e* 274. Other species shown at low *m*/*e* were the fragment ions of the parent ion.

In order to substantiate the difunctionality of the diinitiator made under the aforementioned conditions (i.e. at −20°C and a TEA/*t*-BuLi ratio of 1.5), we have purposely prepared another diinitiator under identical conditions but starting with an excessive amount of *t*-BuLi (at a *t*-BuLi/DIPB molar ratio of 4). The resulting mixture containing the diinitiator and the unreacted *t*-BuLi was used to polymerize styrene. The thus formed polystyrene had a bimodal molecular weight distribution with nearly equal portions of two polymer species having a molecular weight ratio of 2. This observation therefore corroborated the coexistence of difunctionality of the diinitiator and monofunctionality of the *t*-BuLi. (The possible presence of small amount of multifunctional initiators did not affect the molecular weight distribution since they selectively formed difunctional living chains due to a rapid depolymerization of the oligomers upon the monomer addition [45].)

Before synthesizing VBV triblock copolymers using our diinitiator, we needed to explore the proper synthesis



Scheme 2.

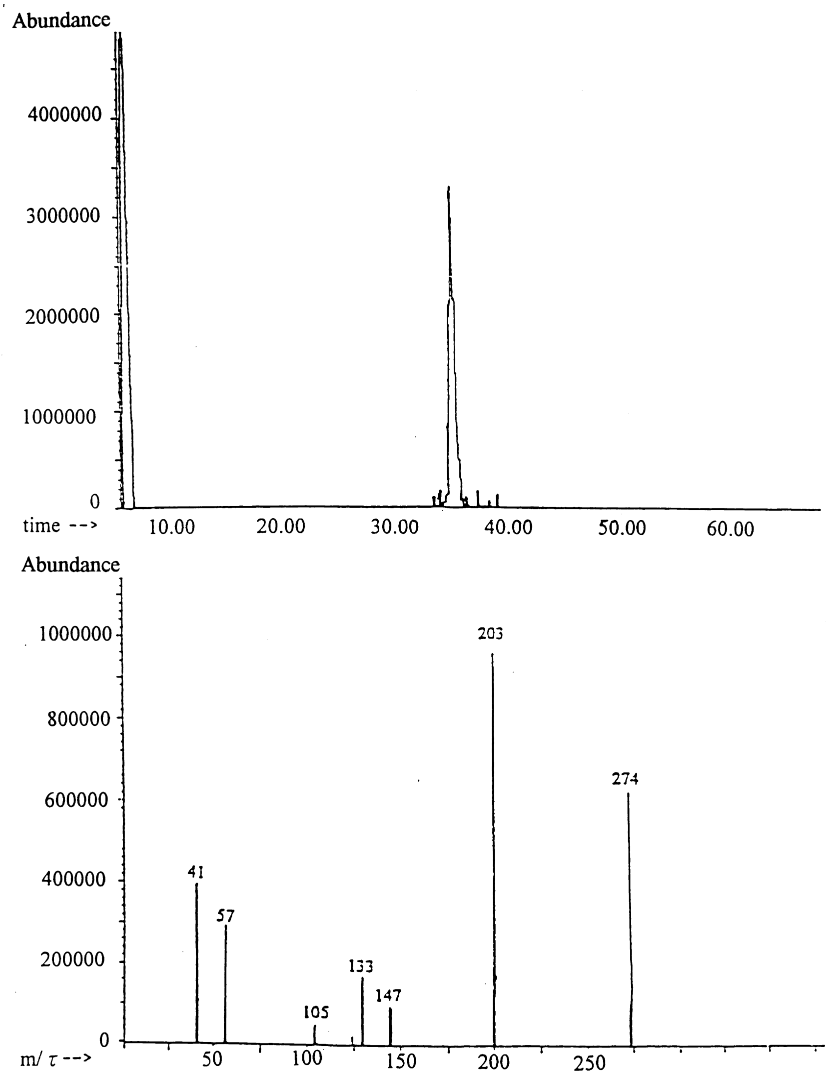


Fig. 2. GC chromatogram and MS spectrum of the diinitiator formed at −20°C.

conditions in order to circumvent the possible side reactions. These side reactions often occurred during the polymerization of 4-vinylpyridine due to its –N=CH– group, and would cause a chain transfer/branching leading to a broader molecular weight distribution [1–3] (Scheme 3).

To facilitate the experimental study on chain branching, the mono-functional initiator, *t*-BuLi, was used to synthesize a polybutadiene-*b*-poly(4-vinylpyridine) diblock copolymer (BV). The purpose was to seek the reaction conditions that enables the formation of a nearly monodispersed, linear BV copolymer.

Experiments were carried out in two different solvent systems, namely cyclohexane and toluene. The resulting GPC chromatograms clearly showed that synthesis at −80°C in the presence of 50 vol% THF enabled the formation of nearly monodispersed BV copolymers regardless of the choice of solvent. The absence of chain transfer/branching has been further verified based on GPC/MALL and UV analysis. The molecular weight of the polybutadiene segment (M^B) was firstly determined by taking a polymer sample out for GPC measurement prior to the addition of 4-vinylpyridine monomer. Next, the weight fraction of the poly(4-vinylpyridine) block in the BV diblock copolymer was calculated utilizing the absorptivity (A_{BV}) determined from our BV diblock copolymer and the absorptivity (A_V) determined from a separately synthesized homopoly(4-vinylpyridine):

$$X_V = A_{BV}/A_V$$

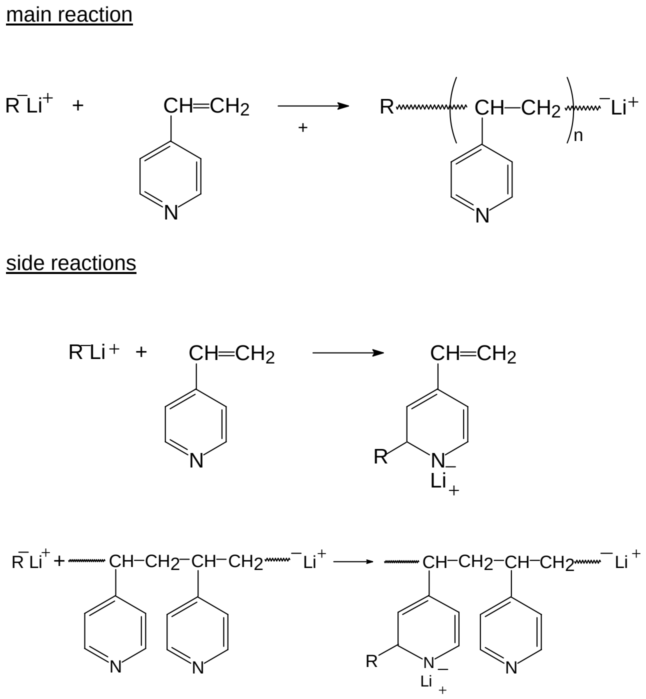
From the X_V and M^B, the molecular weight of the poly(4-vinylpyridine) segment (M^V) could be calculated [3]:

$$M^V = M^B \times (X_V/(1 - X_V))$$

The molecular weight of the BV diblock copolymer could then be calculated as the sum of M^B and M^V

$$M^{BV} = M^B + M^V$$

If the BV copolymer had a linear molecular structure, the



Scheme 3.

observed molecular weight measured by GPC, M_{obs}, should be equal to M^{BV}. Conversely, any nonlinearity of the molecular structure would increase the value of M_{obs}. Data tabulated in Table 1 show that $M_{obs} \approx M^{BV}$, with a relative error of 3%, which is within the range of experimental error, thus corroborating the absence of chain branching under our synthesis conditions. The UV absorption spectra (at 255 nm) of the two BV samples (#1 and #2) and the homopoly(4-vinylpyridine) are shown in Fig. 3.

The temperature effect on the occurrence of side reactions during the formation of the poly(4-vinylpyridine) block has been studied in a toluene/THF (50 vol% each) solvent system. Synthesis at higher temperatures is prone to chain branching, which can be discerned from the existence of a broad, high molecular weight peak in Fig. 4.

After having sought the proper synthesis conditions, our diinitiator was used for the synthesis of VBV. A small amount of butadiene (~2 g) was polymerized by the diinitiator at 40°C in the presence of 25 vol% THF. The conversion of a diinitiator to an oligomeric difunctional living chain reduces the chain ends association and improves the system solubility. The remaining portion of the required amount of butadiene was then added to increase the molecular weight of the polybutadiene. Next, the THF content was increased to 50 vol% and the temperature was decreased to −80°C. The 4-vinylpyridine was then added to continue the polymerization process. The near monodispersity shown by the GPC chromatogram in Fig. 5 clearly indicates an absence of undesirable side reactions.

The stress relaxation characteristics of VBV and analogous SBS triblock copolymers (both having a 70 wt%:30 wt% ratio of rubbery block to hard block as shown in Table 2) have been analyzed and compared via a dynamic mechanical analysis. The curves shown in Figs. 6 and 7 indicate that VBV relaxes slower than SBS when compared at the same temperature. When modeled as a Maxwell element, the relaxation behavior of VBV and SBS copolymers follows an exponential function:

$$\sigma(t) = \sigma_0 \exp\left(-\frac{t}{\lambda}\right)$$

where λ is the relaxation time constant and relates to the activation energy of relaxation, E_a, as follows:

$$\frac{1}{\lambda} = A \exp\left(-\frac{E_a}{RT}\right)$$

The value of λs at various temperatures can be determined from the time required for $(\sigma(t)/\sigma(0)) = e^{-1}$ as shown in Figs. 6 and 7. From the plot of ln λ vs. $1/T$ (shown in Fig. 8 for both VBV and SBS), the E_a can be calculated based on the slope of the fitted line. The thus calculated activation energies of VBV and SBS are 65.8 and 51.9 kJ/mol, respectively. The lower relaxation rate (i.e. the larger activation energy of relaxation) for VBV might arise from a better chain entanglement caused by the hydrogen bonding formed by the electronegative nitrogen atom on the poly(4-vinylpyridine) block.

Phase morphology of VBV and SBS examined by transmission electron microscopy is illustrated in Fig. 9. Domain separation was observed for both copolymers. While the polystyrene in SBS formed small spherical microdomains uniformly distributed in the polybutadiene matrix, the poly(4-vinylpyridine) in VBV, exhibited droplet–cluster microdomains. The difference in morphologies probably results from the ability of poly(4-vinylpyridine) to form

Table 1
Characteristics of BV diblock copolymers (absorptivity of homopoly(4-vinylpyridine) = 3.123)

		Samples	
		#1	#2
B block (measured by MALL)	$M^B \times 10^{-3}$	6.2	9.9
V block (calculated)	$M^V \times 10^{-3}$	2.5	4.6
BV diblock (calculated)	$M^{BV} \times 10^{-3}$	8.7	14.5
BV diblock (measured by MALL)	$M_{obs} \times 10^{-3}$	9.0 (absorptivity = 0.895)	14.0 (absorptivity = 1.003)

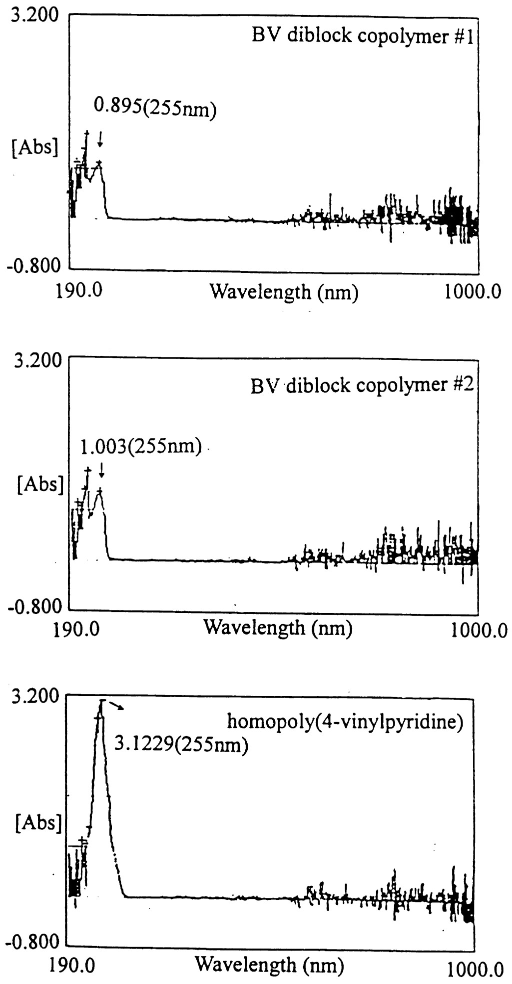


Fig. 3. UV spectra.

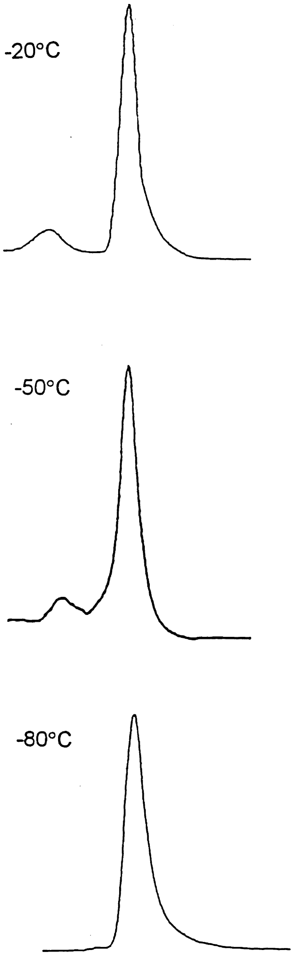


Fig. 4. Effect of temperature on molecular weight distribution of BV diblock copolymers (in a mixed solvent THF:toluene = 1:1 by vol.).

hydrogen bonding, which prevents the microdomains from separating. T_gs of the rubbery phase and the hard phase were observed using a dynamic mechanical analyzer. As shown in Fig. 10, the poly(4-vinylpyridine) phase of the VBV copolymer has a T_g at 135°C and the polybutadiene phase has a T_g of -82°C. In comparison, the SBS copolymer has a 95°C T_g for the polystyrene phase and a -90°C T_g for the polybutadiene phase. Although both copolymers have an equal weight ratio of rubbery phase to hard phase, the T_g of the rubbery phase in the VBV copolymer is increased by approximately 8°C, probably due to the polarity and higher T_g of the poly(4-vinylpyridine) phase.

The relaxation mechanisms for VBV and SBS copolymers have been deduced using the X method [48,49]. The stress relaxation spectrum consists of several discrete time spans:

$$\frac{\sigma(t)}{\sigma(0)} = \sum_{i=1}^{n}\left[\frac{\sigma_i(0)}{\sigma(0)}\exp\left(-\frac{t}{\lambda_i}\right)\right]$$

From the $\ln[\sigma(t)/\sigma(0)]$ vs. t plot, for $t > \lambda_n$ (i.e. the largest relaxation time constant), the back extrapolation of the linear, asymptotic curve yields the values of the intercept and the slope, which by definition are $\ln[\sigma_n(0)/\sigma(0)]$ and $-(1/\lambda_n)$. Next, the item corresponding to the largest relaxation time constant was deducted from the overall spectrum and the $\ln[(\sigma(t)/\sigma(0)) - (\sigma_n(0)/\sigma(0))\exp(-t/\lambda_n)]$ vs. t plot was constructed for the time span $\lambda_{n-1} < t < \lambda_n$. Following the same extrapolation calculation, the values of $\ln[\sigma_{n-1}(0)/\sigma(0)$ and $-1/\lambda_{n-1}]$ were determined. The procedures were repeated to determine the values of other

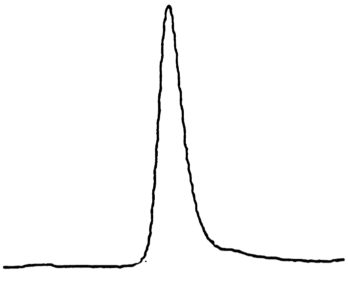


Fig. 5. GPC chromatogram of VBV synthesized at -80°C in a mixed solvent of THF:toluene = 1:1 volume ratio.

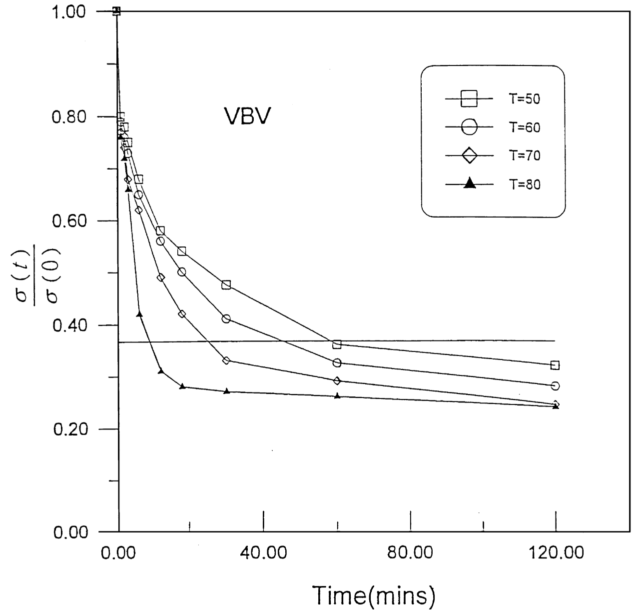


Fig. 6. Stress relaxation curve of VBV at different temperatures.

constants:

$$\ln\left[\frac{\sigma_i(0)}{\sigma(0)}\right] \text{ and } -\frac{1}{\lambda_\mathrm{i}} \qquad \text{for } i = 1,\ldots n-2$$

The stress relaxation mechanism was analyzed at 60°C. The calculated results shown in Fig. 11 indicate that the stress relaxation for VBV and SBS can be described by a spectrum consisting of three time spans:

$$\frac{\sigma(t)}{\sigma(0)} = \frac{\sigma_1(0)}{\sigma(0)}\exp\left(-\frac{t}{\lambda_1}\right) + \frac{\sigma_2(0)}{\sigma(0)}\exp\left(-\frac{t}{\lambda_2}\right) + \frac{\sigma_3(0)}{\sigma(0)}\exp\left(-\frac{t}{\lambda_3}\right)$$

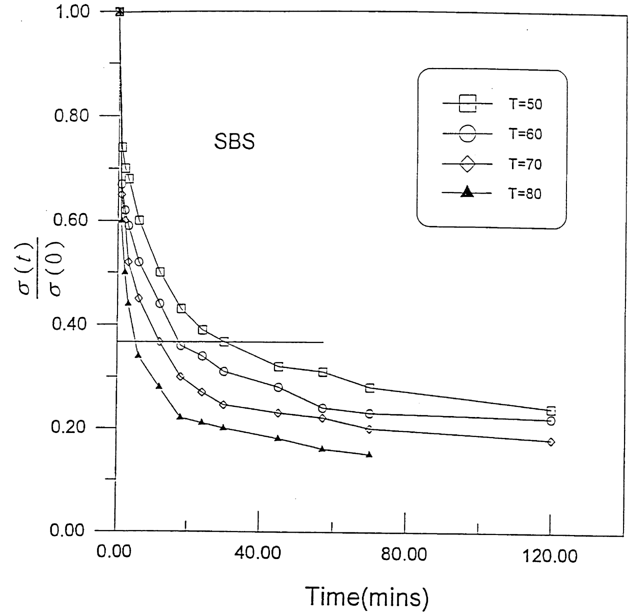


Fig. 7. Stress relaxation curve of SBS at different temperatures.

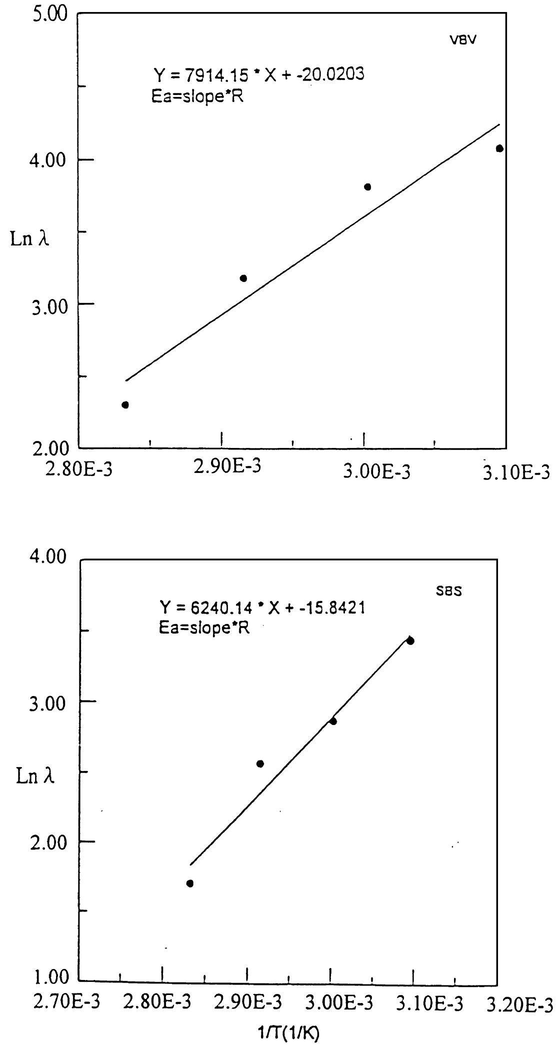


Fig. 8. lnλ vs 1/T plot for calculating the activation energy.

These three time spans correlate to the three major mechanisms of stress relaxation, namely physical flow, physical untanglement, and domain destruction [37,39]. The physical flow occurs first upon an applied stress, followed by the physical untanglement and domain destruction at larger time scales. The calculated constants for VBV and SBS copolymers are tabulated in Table 3. The initial stresses for both VBV and SBS are in such order:

$$\frac{\sigma_1(0)}{\sigma(0)} > \frac{\sigma_3(0)}{\sigma(0)} > \frac{\sigma_2(0)}{\sigma(0)}$$

indicating that the relaxation by physical flow is greater than

Table 2
Characteristics of VBV and SBS compared in this work

	% Butadiene	% Hard block	M_w	M_n	MWD
VBV	70	30	34,913	33,263	1.05
SBS	70	30	43,720	41,350	1.06

Table 3
Constants of the stress relaxation spectra for VBV and SBS

	$\sigma_1(0)/\sigma(0)$	$-1/\lambda_1$	$\sigma_2(0)/\sigma(0)$	$-1/\lambda_2$	$\sigma_3(0)/\sigma(0)$	$-1/\lambda_3$
VBV	0.41	− 0.21	0.21	− 0.026	0.38	− 0.002
SBS	0.52	− 0.23	0.16	− 0.033	0.32	− 0.0019

that by domain destruction, which in turn is greater than that by physical untanglement.

4. Conclusions

A diinitiator, prepared by reacting 2 mol of *t*-BuLi with 1 mol of DIPB at −20°C with a 1.5 molar ratio of TEA to *t*-BuLi, was used to synthesize a linear, nearly monodispersed poly(4-vinylpyridine)-*b*-polybutadiene-*b*-poly(4-vinylpyridine) (VBV) with great success. The synthesis was conducted at −80°C in a mixed THF/toluene solvent in order to circumvent the chain branching reactions arising

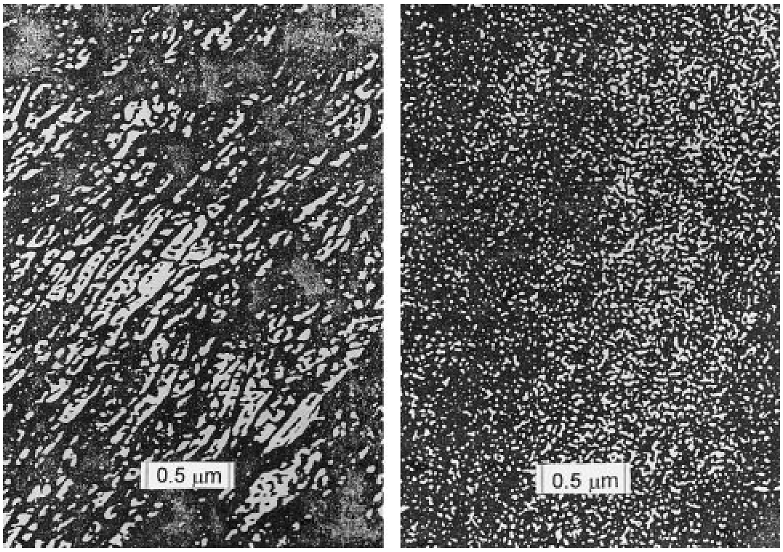


Fig. 9. TEM micrograph for VBV and SBS (left: VBV, B/V = 70%/30%, $M_w = 34{,}913$, polydispersity = 1.05; right: SBS, B/S = 70%/30%, $M_w = 43{,}720$, polydispersity = 1.06).

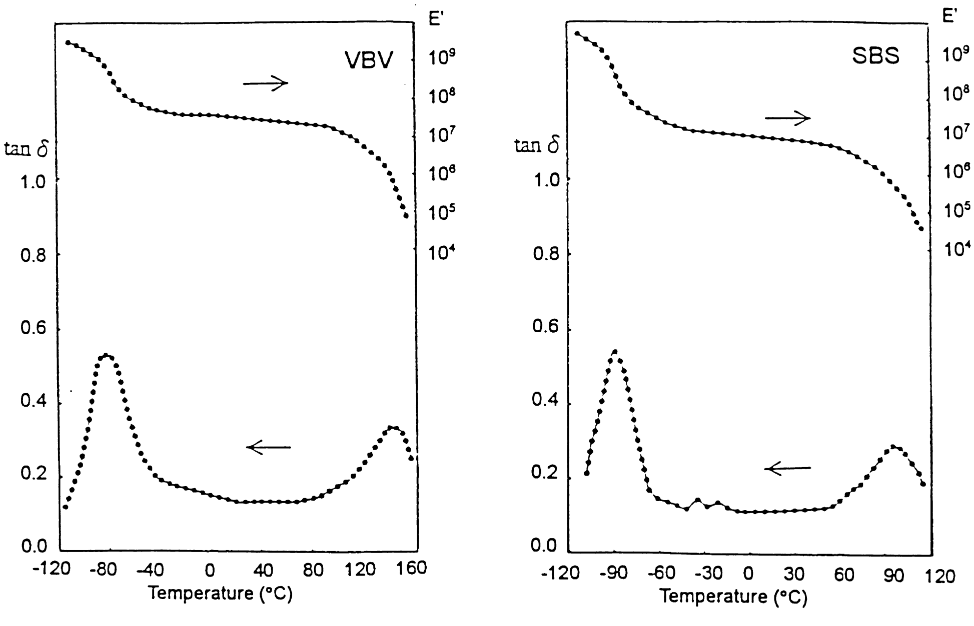


Fig. 10. Dynamic mechanical behavior of VBV and SBS.

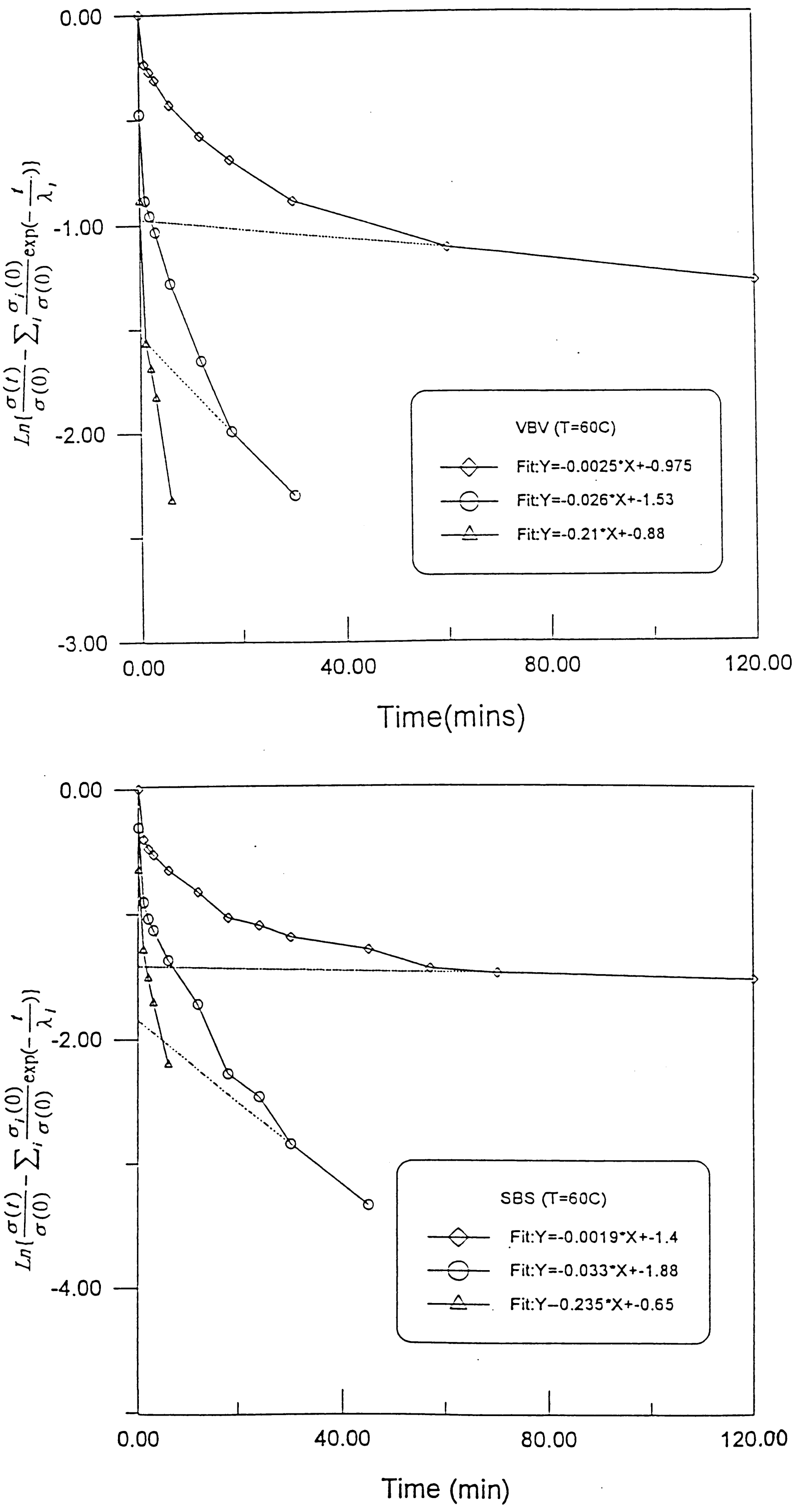


Fig. 11. Stress relaxation calculation based on X-method at 60°C.

from the –N=CH– group of the 4-vinylpyridine. The absence of chain branching under such conditions has been verified by GPC/MALL and UV analyses, and syntheses at higher temperatures have been detrimental. Compared with the polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS), VBV relaxes slower with a higher activation energy of relaxation. Whilst phase separation occurs for both VBV and SBS, VBV exhibits a different morphology having a droplet–cluster hard domain. The polarity of the poly(4-vinylpyridine) not only increases the T_g of the hard block, but also increases the T_g of the rubbery polybutadiene phase. The relaxation mechanism deduced based on the X-method has shown that contributions to relaxation by physical flow is greater than that by domain destruction, which in turn is greater than that by physical untanglement.

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